



A novel aluminium-air semi-fuel cell operating with hydrogen peroxide co-generation

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HIGHLIGHTS

- The possibility of generation of H₂O₂ in original system of Al-air SFC was shown.
- It was study operation of different types of cathodes and ion-exchange membranes.
- Hydrogen peroxide was obtained by a rate 58.3 mg h⁻¹ cm⁻² by 85% current efficiency.
- It was shown 15-times (electrode area 100 cm²) scaled up Al-air SFC.
- Al-air SCF can generated H₂O₂ in diluted water (30 g l⁻¹ NaCl as a catholyte).

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ABSTRACT

An original Al-air semi-fuel cell (SFC) system, operating with hydrogen peroxide (H₂O₂) co-generation was developed. The cell design was optimized and operating conditions were selected in the comparative study of different of anion-exchange MA-40, AMI 7001S and cation-exchange MK-40, NAFION 117 membranes, gas-diffusion electrodes (GDE) Black Pearls 2000 (BP 2000), Vulcan XC-72 (XC-72), nature and concentration of electrolytes (NaOH, KOH and NaCl). Their influence on electric characteristics (current density and generated power) and current efficiency of H₂O₂ generation was studied. The best results were achieved were using BP 2000 GDE in the SFC divided by anion-exchange membrane (AEM) with 6M KOH as an electrolyte. However, some acceptable results were achieved even using dilute chloride solutions. Finally, the scale-up experiments showed that the specific electric characteristics of the fuel cell (FC) enhanced at 15-fold increase of the electrode area.

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1. Introduction

Hydrogen peroxide and hydroxyl radicals (*OH), formed in-situ due to catalytic action with of Fe(II) salts, ozone or UV irradiation on diluted solutions of H₂O₂ are attributed to a “green reagents” group as they are decomposed in ox-red reactions only to environmentally friendly products - water and oxygen. Due to oxidative ability ($E^0 = 1.7$ V), antiseptic and anti-bacterial properties of H₂O₂ is widely used in textile, pulp and paper, detergents, cosmetic industries and in medicine while application of *OH ($E^0 = 2.8$ V) is a basis of advanced oxidation processes (AOPs) for effective

treatment of water, contaminated by non-biodegradable aromatic organic substances.

Industrial manufacturing of H₂O₂ is currently based on so called “anthraquinone” process which needs huge centralized hydrogen production plants for the feedback and therefore is located at several sites, usually far from consumers. Delivery, storage and handling of hazardous concentrated solutions of the strong oxidant is costly and risky, especially for agricultural, touristic, exploring and military objects and individuals, operating in remote regions (mountains, deserts, marine, etc.) and insulated (underwater, space) systems. That makes development and implementation of the compact, environmentally acceptable and economically profitable, energetically self-sufficient devices for the on-site generation of safe diluted H₂O₂ solutions an important issue.

Electro-synthesis of H₂O₂ by means of the two-electron electrochemical reduction of oxygen at carbon cathodes appears to be

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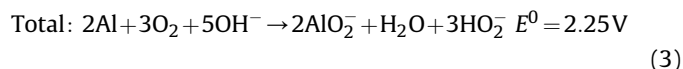
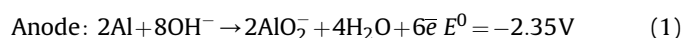
¹ “ISE member”.

a good alternative to the “anthraquinone” method (1, 2). Due to limited solubility of oxygen in water a variety of electrochemical reactors with an expanded surface area electrodes (gas-diffusion, packed bed, carbon felt and etc.), fed from the outer source of a direct current were tested in recent comprehensive studies [1–9].

Possibility of H_2O_2 generation in the direct methanol fuel cell (DMFC) and direct borohydride fuel cell systems was shown in our previous publications [10,11]. These FCs, based on oxidation of alcohols are more energy-saving, safe and convenient in operation in comparison with small-scale FC systems, where hydrogen was used as a fuel [12]. Application of solid state reducing agent instead of gaseous or liquid fuels appears to be even more convenient for storage, transportation and handling in the field conditions.

Aluminium, an abundant and relatively inexpensive metal, is a very attractive anode material for energy storage and conversion in primary batteries and SFCs due to its relatively low weight and a high electrochemical equivalent of 2.98 Ah g^{-1} , compared with 0.82 Ah g^{-1} for zinc which is widely used in energy sources. From a volume standpoint, aluminium should yield 8.04 Ah cm^{-3} , compared with 2.06 Ah cm^{-3} for lithium, 5.85 Ah cm^{-3} for zinc and 3.83 Ah cm^{-3} for magnesium. Appearance of the protective oxide film on aluminium metal causes a decrease in the reversible electrode potential and usually the cell voltage is considerably lower than the theoretical value [13].

The goal of the present work consists in development of the novel Al-air SFC system with 2.25 V open circuit voltage, maintaining Al oxidation at the anode and two-electron oxygen reduction reaction (ORR) at the cathode (Eqs. (1)–(3)) [14], based on a study of influence of composition and concentration of tested alkaline and chloride electrolytes, properties of used gas-diffusion cathodes and ion-exchange membranes on electric characteristics and HO_2^- generation current efficiency, effect of ranging from the small size cell to 15 times scaled-up FC system.



2. Experimental

Two type GDEs – commercial “A12H2O2 specialty ELAT® GDE for Hydrogen Peroxide” with XC-72 carbon black active layer, supplied by E-TEK Inc. (USA) and a noncatalyzed BP 2000 carbon-PTFE layer electrode, supplied by Electro-Cell AB (Sweden) were tested for ORR maintaining (Eq. (2)). The composition of the used anode material, determined by “INNOV-X SYSTEMS” Delta-Analyzer was: Al – 99.4%; Fe – 0.28%; Si – 0.17%; Cr – 0.01%; Ni – 0.002%; Zn – 0.007%. Anion-exchange membranes – MA-40 (produced by NPO “Schekino,” Russia), AMI 7001S (Membranes International, Inc., USA) and cation-exchange membranes – MK-40 (Russia) and Nafion® 117 (Du Pont, USA) were tested for the separation of anode and cathode compartments.

All solutions were prepared using distilled water and chemical grade reagents. Measurements of current, voltage and pH were carried out using M2015 ammeter, M106 high-impedance voltmeter and HI 8424 microcomputer pH-meter, accordingly. The concentration of HO_2^- , accumulated in the electrolyte was determined by standard titration method with KMnO_4 . The OH^- concentration was determined by titration with standardized 1 mol dm^{-3} HCl solution [15,16].

The experimental setup is shown in the Fig. 1. Anolyte and catholyte solutions were circulated through the anode and cathode

compartments of the Al-air SFC 1 to the corresponding tanks 2, 3 by means of pumps 4. Pressure of air, fed from the air-pump 5 to the gas chamber was controlled by manometer 6. The external load was changed using a box of resistors R, and the FC parameters were controlled by an ammeter and a high impedance voltmeter [17].

Detailed drawing of the used cell components is shown in the Fig. 2. End plates 1 and 2, gas-diffusion cathode 3 with nickel mesh 4, served as a current feeder, and gas chamber 5 for air supply, aluminium anode 6, fixed in methyl-acrylate frame, spacers 7, served for catholyte and anolyte supply, ion-exchange membrane 8 and rubber gaskets 9 were fixed in a filter-press type cell.

3. Results and discussion

3.1. Small size Al-air SFC performance

3.1.1. Effect of composition and concentration of alkaline electrolytes

Current–voltage characteristics of the Al-air SFC with GDE of 6.7 cm^2 surface area and aluminium anode of 9 cm^2 area, recorded in tests with 1 M NaOH and 1 M KOH electrolytes changing resistance of the outer load in ($10^4 \Omega$ – $10^{-1} \Omega$) range are shown in Fig. 3.

Higher values for generated power (17.1 mW cm^{-2}) and current density (53 mA cm^{-2}) were achieved in tests with 1 M KOH electrolyte while in the case of 1 M NaOH maximum power was only 10.44 mW cm^{-2} and current density decreased to 31 mA cm^{-2} . Maximum generated power increased in two times with a rise of current density in 2.1 times when the electrolyte concentration was increased from 1 M to 6 M KOH (Fig. 4). This can be explained by the higher specific conductivity of potassium hydroxide electrolyte in comparison with sodium hydroxide and by a rise of specific conductivity of the electrolyte from $(2.723 \times 10^{-7}) \Omega^{-1} \text{ cm}^{-1}$ for 1 M KOH to $(5.221 \times 10^{-7}) \Omega^{-1} \text{ cm}^{-1}$ for 6 M KOH, and consequent decay of conductivity for 8 M KOH solutions. The voltage drop is minimal in 6 M KOH solution that determines high current density and correspondingly, high rate of H_2O_2 electro-generation in the catholyte. On the other hand, precipitation of carbonates due to absorption of CO_2 by the alkaline solution in pores of the gas-diffusion electrode leads to relative reduction of rate and current efficiency of H_2O_2 generation. Therefore, in the case of potassium carbonate which is much more soluble in water than sodium carbonate, pores of the GDE were not blocked by the precipitated Na_2CO_3 , the entire electrode area for the ORR was larger, cell worked more stably and generated more power [5].

3.1.2. Influence of a gas-diffusion cathode nature on current–voltage characteristics

Performance of two different types of commercial O_2 -gas-diffusion cathodes—XC-72 and BP 2000 of the similar sizes (6.7 cm^2 geometric area) were compared in following tests to solutions of 2 M KOH, used both as an anolyte and a catholyte, separated by MA-40 anion-exchange membrane. Air was supplied to the GDE under 350 Pa pressure.

As is evident from the Fig. 5, in the case of BP 2000 maximum 17.16 mW cm^{-2} power and 53 mA cm^{-2} current density were achieved while at XC-72 cathode these indications comprised 15.9 mW cm^{-2} and 49 mA cm^{-2} , accordingly. So, despite the significant difference in porosity of commercial gas-diffusion cathodes (1 g of BP 2000 covers 1475 m^2 while the same amount of XC-72 carbon black comprises 254 m^2 surface area), electric characteristics of both electrode materials do not differ significantly.

3.1.3. Influence of membrane nature

Different type AEM and cation-exchange membrane (CEM) were tested for separation of the anolyte and the catholyte (100 ml 1 M

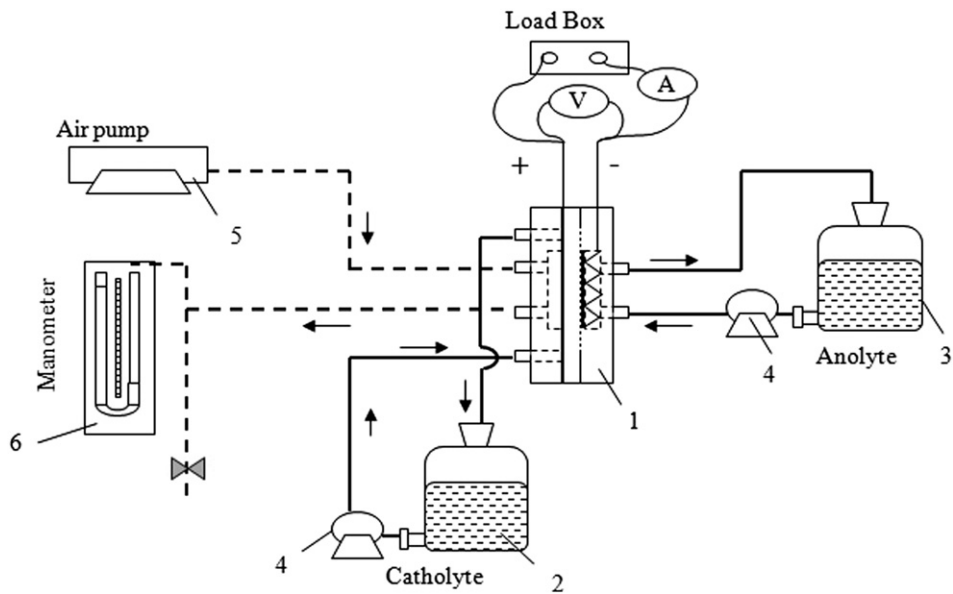


Fig. 1. Experimental setup.

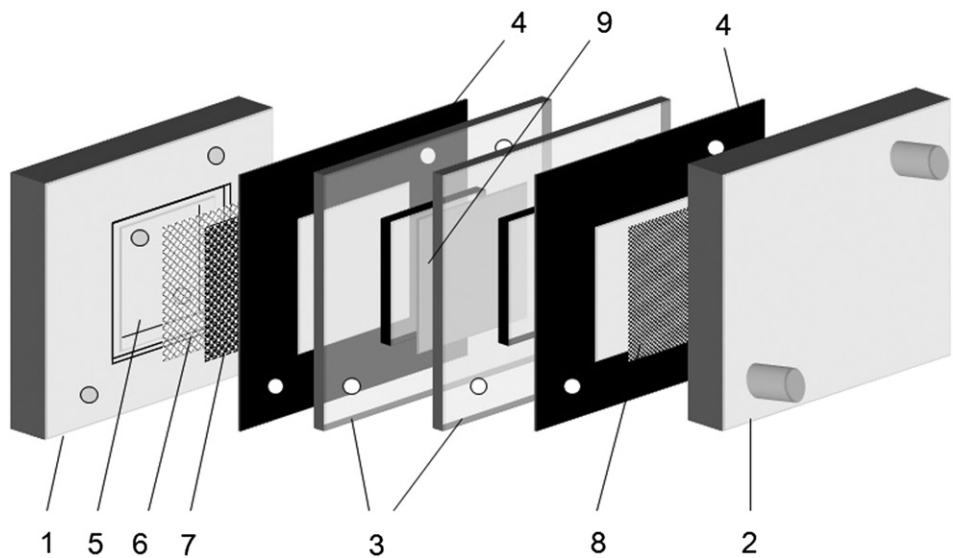


Fig. 2. Principal scheme of the Al-air SFC for hydrogen peroxide cogeneration.

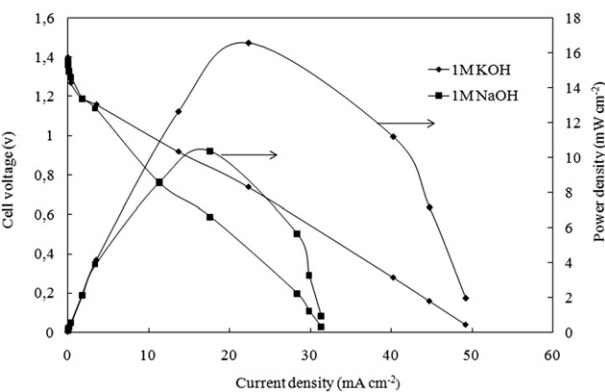


Fig. 3. Dependence of the SFC electrical properties on the electrolyte type with 1 M NaOH and 1 M KOH.

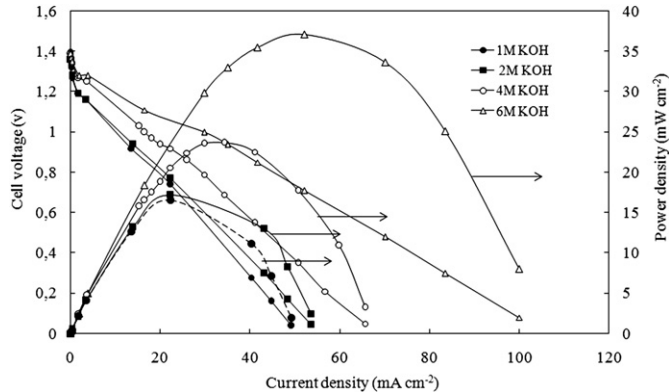


Fig. 4. Variation of the SFC electrical properties with KOH concentration in the electrolyte.

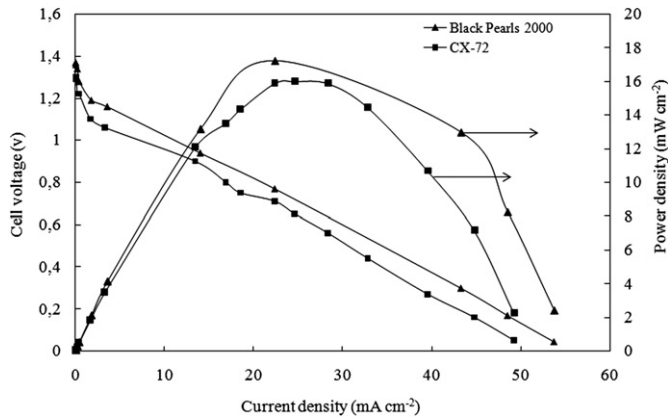


Fig. 5. Influence of cathode type on the SFC electrical properties.

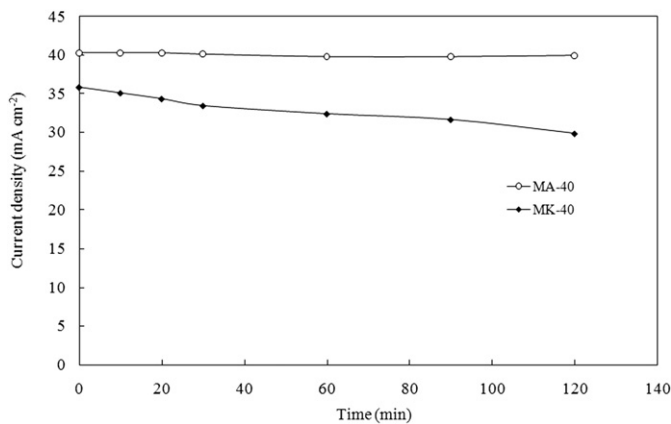


Fig. 6. Comparison of the SFC generated current with time in trials with different type of ion-selective membranes.

KOH each) in small scale Al-air cell connected to 0.1 Ω outer resistance. Test results are illustrated in the Figs. 6 and 7.

In the case of MA-40 type AEM, an application of stable generation of 40.3 mA cm⁻² current (Fig. 6) and 100% current efficiency of H₂O₂ generation (Fig. 7), was achieved at the earlier stage which

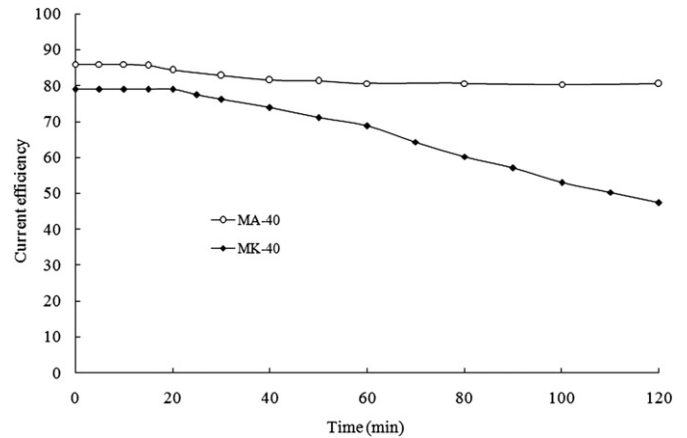


Fig. 7. Variation in H₂O₂ CE with time in trials with different type of ion-exchange membranes.

reduced to 85% after 2 h. These data are in correlation with those obtained in our tests of H₂O₂ generation in the cell with outer power supply and slight fall of current efficiency can be explained by the known effect of elevated decomposition of the product when H₂O₂ concentration increases in time. This negative effect can be eliminated if all generated HP will be instantly used for treatment of the polluted water and concentration of the product will be low continuously the in-cell treatment process [7].

In tests with MK-40 type CEM, generated current decreased from 35.8 mA cm⁻² to 29.85 mA cm⁻² (Fig. 6), and the H₂O₂ current efficiency dropped from initial 80%–45% in the second hour of operation (Fig. 7). Obviously internal resistance of the cell increased as concentration of alkali decreased in time due to constant migration of K⁺-ions through the CEM from the anolyte to the catholyte where they were connected with products of reaction (Eq. (3)) (Fig. 8).

In the case of AEM application, stable balance of ions was achieved at both sides of the membrane. OH⁻ ions, which generated at the cathode, penetrate through the CEM and take part in Al oxidation reaction.

Based on the results of the comparative study all following experiments were performed using AEMs for separation of anode and cathode compartments of the FC.

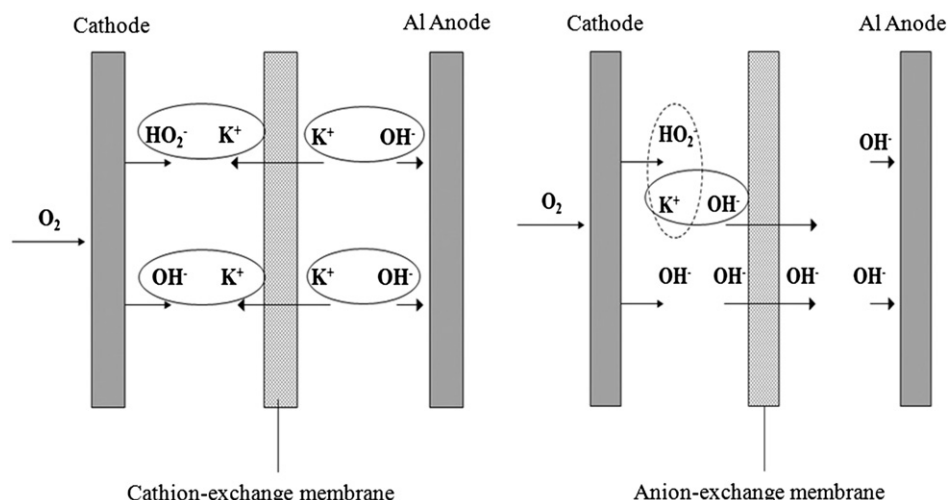


Fig. 8. Illustration of ions migration in the SFC with anion- and cation-exchange membrane.

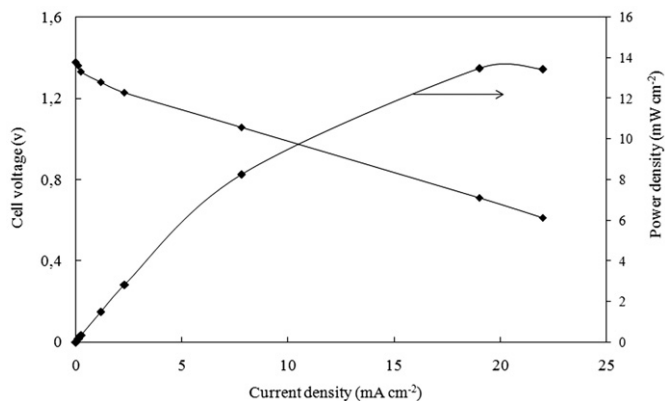


Fig. 9. Electrical properties of the SFC with 1 M NaOH electrolyte.

3.2. Scale up experiments

Al-air SFC of the similar to small scale cell shape, with 100 cm² surface area for each electrode, BP 2000 type GDE, used as a 15-times enlarged cathode and 11-times enlarged aluminium plate as an anode, was developed for further experiments. Anion-exchange membranes AMI 7001 S (USA), MA-40 (Russia) and cation-exchange membrane Nafion[®] 117 (USA) were used for separation of anode and cathode chambers in different trials.

In tests, performed with sodium hydroxide electrolyte, increasing of the anode and the cathode active area size causes an improvement of current–voltage characteristics of the fuel cell. Maximum value for power of 14 mW cm^{−2} was achieved in the enlarged cell in comparison with 10.4 mW cm^{−2} for the small size FC and corresponding values for current density were 23 mA cm^{−2} (Fig. 9) and 17 mA cm^{−2} (Fig. 3). Current efficiency of H₂O₂ decreased from 82% to 77.5% after 180 min (Fig. 10) due to increased decomposition of the product with accumulation of the H₂O₂ in the circulated solutions, though generated current was stable in time [10,11].

Current–voltage parameters of Al-air SFC with 30 g L^{−1} NaCl solution as a catholyte and 6 M NaOH as an anolyte are shown in Fig. 11. The FC was separated by AMI 7001S and MA-40 membranes. In the case of MA-40 the FC generates maximum power 15.43 mW cm^{−2} at 24 mA cm^{−2} current and H₂O₂ current efficiency was changed, during 180 min, from initial 80% until 69% and in the case of AMI 7001S maximum power 9.48 mW cm^{−2} was reached at 16 mA cm^{−2} current, but the product current efficiency 80% was stable in time Fig. 12.

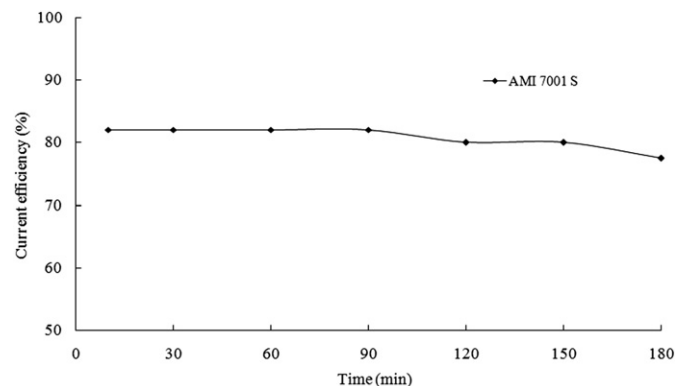


Fig. 10. Variation of the SCF generated H₂O₂ current efficiency in time with 1 M NaOH electrolyte.

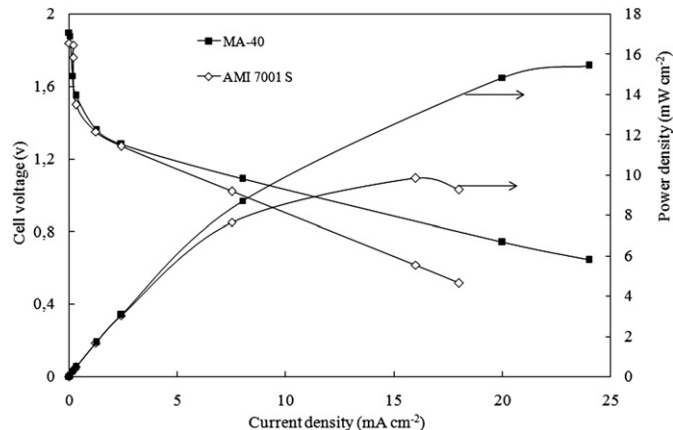


Fig. 11. Influence of anion-exchange membranes type on the electrical properties of the SFC.

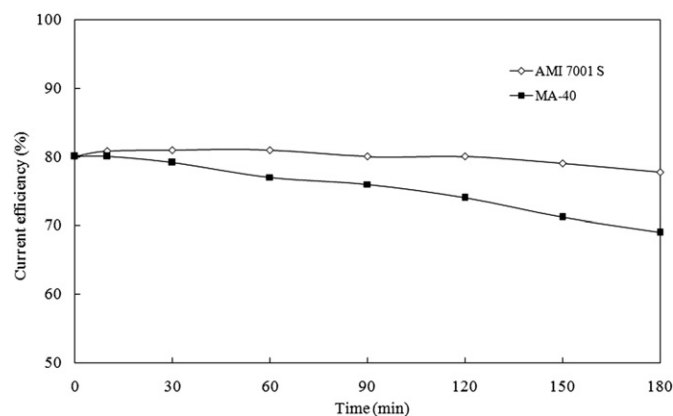


Fig. 12. Variation of the SCF generated H₂O₂ current efficiency in time, with different type of anion-exchange membrane.

In the next tests 30 g L^{−1} and 150 g L^{−1} NaCl solutions were used as a catholyte and as an anolyte, accordingly. Fig. 13 illustrate that when alkaline anolyte was replaced by chlorine solution the Al-air FC parameters were dropped almost 3 times. However, chlorine solution is cheap and application areas of the fuel cell could be increased. From used two type membranes, AMI 7001S must be preferable since H₂O₂ current efficiency is stable for 180 min and

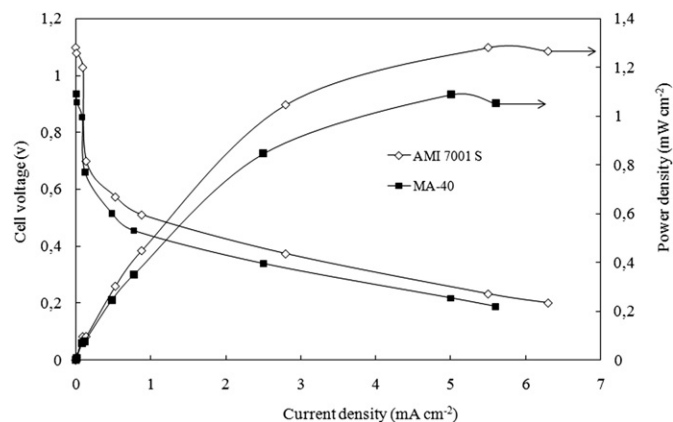


Fig. 13. Influence of anion-exchange membranes type on the electrical properties of the SFC, with 30 g L^{−1} catholyte and 150 g L^{−1} NaCl anolyte.

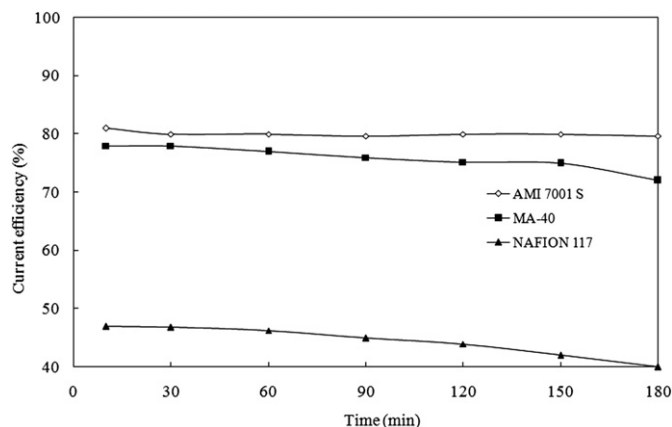


Fig. 14. Variation of generated H_2O_2 current efficiency in time, with different type of anion-exchange membrane (AMI 7001S and MA-40) and cation-exchange membrane Nafion[®] 117.

reaches 80%. In the case of MA-40, H_2O_2 current efficiency changes from 79% to 72% for the same time of tests.

The neutral medium was maintained at the use of CEM Nafion[®] 117 (Fig. 14) in the FCs anolyte, and the alkaline content in catholyte increased (similar fact was also observed in small-size reactor); H_2O_2 current efficiency was varied in the range of 40–47%.

4. Conclusion

The possibility of electro-generation of H_2O_2 with stable electric characteristics in original system of Al-air FC was shown. The effect of various factors—electrode and membrane material, electrolyte consist, its concentration and temperature — on electric characteristics of this system and on product was studied. It was established that in small-size cell ($S_c = 6.7 \text{ cm}^2$) the power was varied from 0.058 mW cm^{-2} to 8 mW cm^{-2} at the variation of outer resistance from $10^4 \Omega$ to $10^{-1} \Omega$ and at the use of BP 2000 as cathode material, 1 M KOH as an electrolyte and MA-40 as AEM. Maximum density of generated current comprised 100 mA cm^{-2} . Hydrogen peroxide was obtained by a rate $58.3 \text{ mg h}^{-1} \text{ cm}^{-2}$ by 85% current efficiency.

The possibility of the transition to large-scale cell was shown. If in small-size plant the maximum specific power comprised

10.4 mW cm^{-2} , at current density of 17 mA cm^{-2} , then at 15-fold increase of electrode surface the maximum specific power comprised 14 mW cm^{-2} which was fixed at current density of 23 mA cm^{-2} . H_2O_2 current efficiency comprised 82% in initial period in the cell of enlarged-size. After 90 min the current efficiency decreased and attained 77.5% after 180 min.

The possibility of the use of sodium chloride as an electrolyte in FCs also was established. In salt current sources the electric capacity reduces approximately twice in comparison with alkaline cells. This fact provides definite advantages for consumers since they are cheap, available and safe in service, especially in operation of sea and coast conditions.

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